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U. S. Army
Chemical Research and Development Laboratories
Technical Report

CRDLR 3161

Methods of Microanalysis, VIc
Oxygen Determination; The Platinum-Tube Method for
Fluorine-Containing Compounds
(A Preliminary Investigation)

by
Stewart S. Cruikshank

February 1963



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OXYGEN DETERMINATION; THE PLATINUM-TUBE METHOD FOR
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FOREWORD

The work covered in this report is intermittent work commenced on 7 June 1957 and suspended on 18 July 1961 under Task 4C08-03-016-08, Analytical Chemical Research (U). The experimental data are recorded in notebooks DO-3, DO-7, and Fluorocarbon C&H — serial designations A and B.

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DIGEST

The work leading to this report is part of a research program designed to result in improved microanalytical methods. A previous report of this series shows a greatly improved temperature control for the main furnace used in the oxygen determination. Another report shows the failure of magnesium nitride as a method to eliminate interference by fluorine. The present report describes progress to date with a platinum pyrolysis tube in place of the customary quartz tube to determine oxygen in fluorine-containing compounds.

The platinum-tube method devised here shows good promise for eliminating the interference of fluorine in the oxygen determination. Further work is planned with other compounds and with carbon thoroughly purified before placing it in the platinum tube.

CONTENTS

	<u>Page</u>
I. INTRODUCTION	5
II. EXPERIMENTAL	7
A. Equipment, Materials, and Operation	7
B. First Trial	10
C. Second Trial	11
III. DISCUSSION	12
IV. CONCLUSIONS	13
LITERATURE CITED	15

METHODS OF MICROANALYSIS, VIc
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I. INTRODUCTION.

Originally, oxygen present in organic compounds was determined by difference; that is, by subtracting the sum of all the other elements determined from 100%. Obviously, this was not very accurate or dependable since the sum of the errors of other determinations accumulated in the oxygen value. Amounts under 1% oxygen could hardly be attempted. Sometimes another element was present which was not known and, therefore, no analysis was performed for it. The percentage of this unknown element was included in the oxygen value reported. In some instances, such as certain purification and surveillance experiments, the exact amount of oxygen present is of far more interest than the amounts of the other elements present.

A hydrogenation type of direct oxygen determination was devised by ter Meulen¹ in 1934 and improved by Linder and Wirth² in 1937. This hydrogenation method has never been widely used, even though many people tried to improve it, because the results tend to be low and several common elements interfere.

The pyrolysis and conversion of all oxygen to carbon monoxide was reported by Unterzaucher³ in 1940. In this method, the fragments of the organic molecule are led through carbon which should be kept at $1,120^{\circ} \pm 5^{\circ}\text{C}$ for complete reduction to carbon monoxide. A greater variation in the operating temperature will give a high blank. Unterzaucher gives his blank determination as nil.

The Unterzaucher method was investigated and discussed by Aluise, Alber, Conway, Harris, Jones, and Smith⁴ in 1951. They recommend the method, with close control of temperature, but believe some blank is inevitable under ordinary operating conditions. (See figure 1.)

Various modifications have been reported, such as diffusing hydrogen through porous palladium, adding a section of hot copper to eliminate interference by sulfur, absorbing and weighing the carbon dioxide or iodine, using palladium sulfate as a colorimetric indicator^{5, 6} and others. However, none of these is an attempt to avoid interference by fluorine.

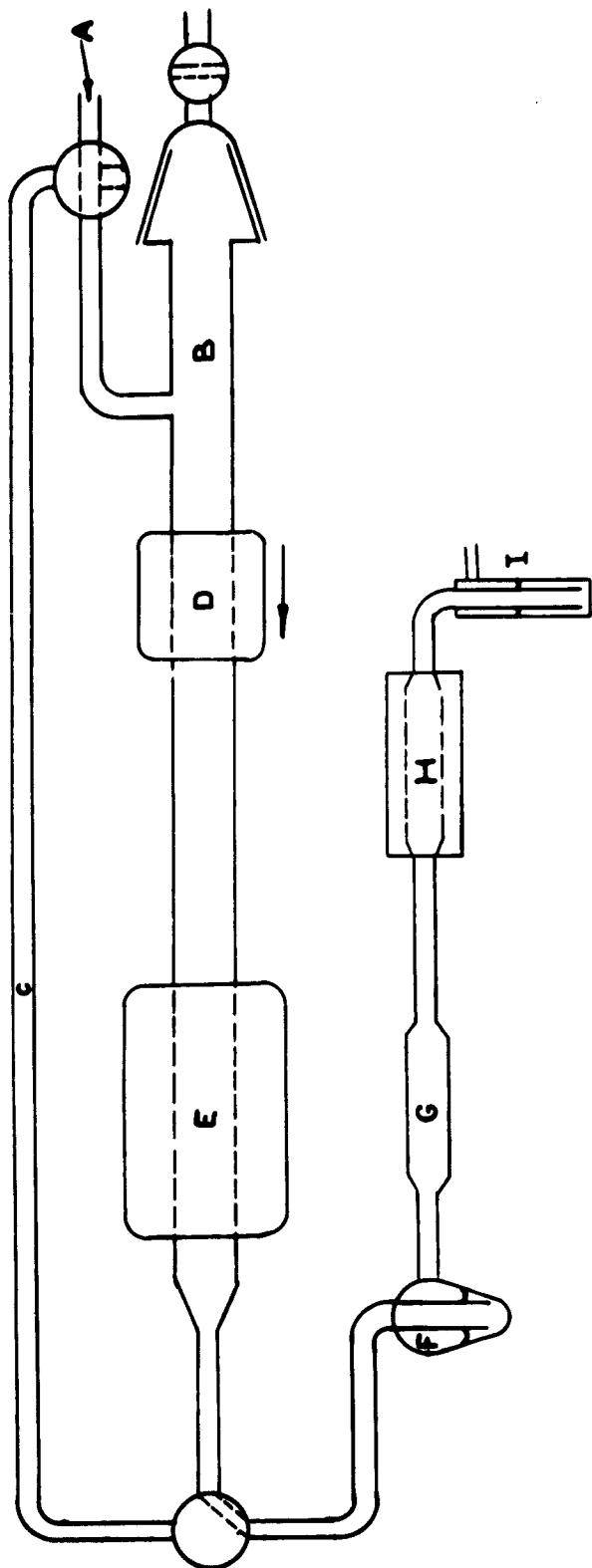


FIGURE 1
SCHEMATIC DIAGRAM FOR DIRECT OXYGEN APPARATUS

(A) Entrance for purified, dried helium or nitrogen, (B) pyrolysis tube, (C) bypass, (D) cylindrical burner operating at $1,100^{\circ}\text{C}$, (E) main furnace - carbon at $1,120^{\circ}\pm 5^{\circ}\text{C}$, (F) sulfuric acid bubbler, (G) Ascarite, (H) iodine pentoxide at 110°C , and (I) absorber.

There are not many elements which interfere with the pyrolysis method. Fluorine reacts with the quartz tube and gives high results,^{3,4,7,8,9} phosphorus usually causes low results, and sulfur causes slightly high results. Hydrogen is stated by some authorities to interfere to some extent. The interference of hydrogen, phosphorus, sulfur, and metals will be discussed in a subsequent report. Aluminum and alkaline earth metals retain oxygen as metallic oxides; alkali metals hold only a small amount of oxygen.

The magnesium nitride method⁸ was investigated in this laboratory⁹ but it failed and was abandoned. The extent of interference by fluorine when using a quartz tube is shown in another report.⁹

Magnesium oxide surrounding the sample which is placed in a capsule has been proposed as a method.¹⁰ Under the proper conditions, the fluorine would release oxygen from the magnesium oxide which would be determined in addition to oxygen coming directly from the sample. Fluorine, determined separately, could then be deducted and the true oxygen result would be determined by difference. It seems obvious that other halogens and phosphorus would interfere.

II. EXPERIMENTAL.

A. Equipment, Materials, and Operation.

The oxygen train is that of the Arthur H. Thomas Co., with modifications described in a previous report.¹¹ See figure 2 of that report and figure 1 of this report.

The platinum tube was made according to figure 2 by Baker Platinum Division of Englehard Industries, Inc. It is longer than the customary quartz tube and somewhat thicker.

Platinum boats, 13 mm in length, 5 mm in width, 4 mm in depth

A longer bypass and twice as many supports

Carbon black, pelletized Huber, Arthur H. Thomas Co.

Acetanilide, National Bureau of Standards

Benzoic acid, National Bureau of Standards

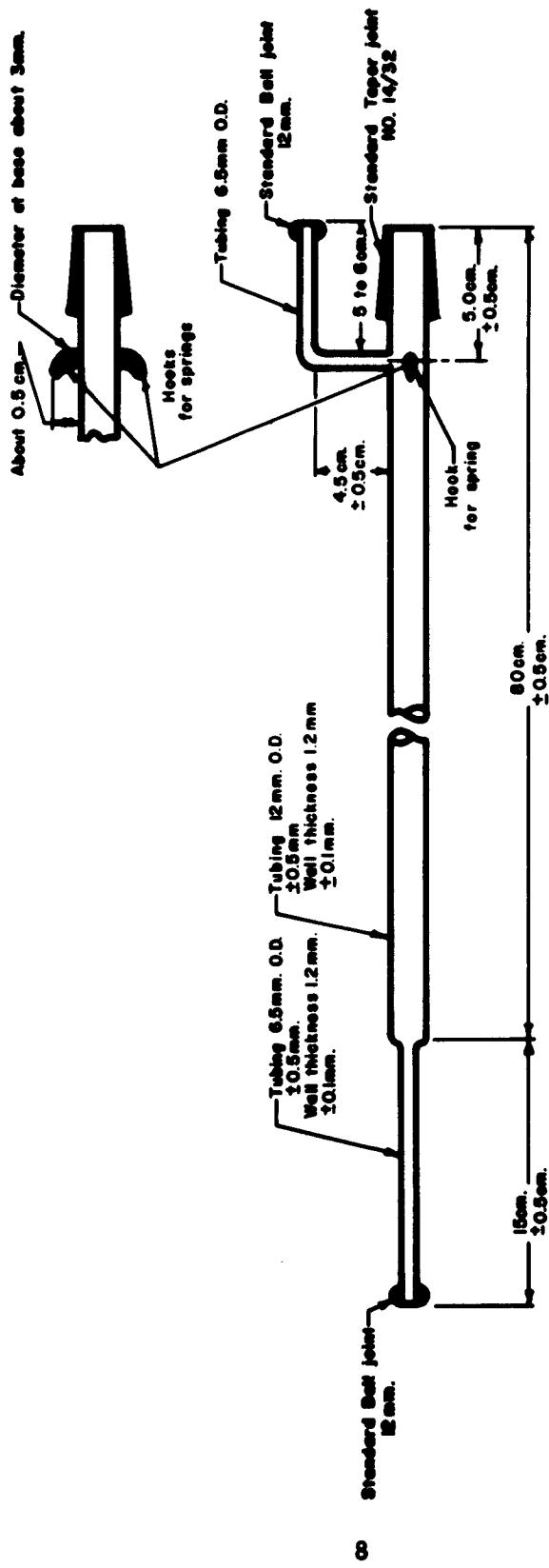


FIGURE 2
PLATINUM PYROLYSIS TUBE

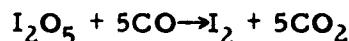
Perfluorodibutyl ether, purified in this laboratory by repeated distillations

Teflon, commercial plastic, judged pure by carbon and hydrogen analysis

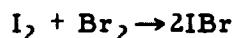
Hydrogen fluoride gas (not analyzed), Pennsylvania Salt Co.

Hydrofluoric acid, 48% reagent, General Chemical Division, Allied Chemical and Dye Corp.

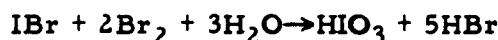
In the Unterzaucher method, the organic compound is pyrolyzed in an inert atmosphere such as pure nitrogen or helium. See figure 1. Resulting fragments are carbon dioxide, carbon monoxide, water, nitric oxide, nitrogen dioxide, sulfur dioxide, sulfur trioxide, oxygen, ammonia, hydrogen, fluorine, hydrogen fluoride, chlorine, hydrogen chloride, bromine, hydrogen bromide, iodine, hydrogen iodide, hydrogen sulfide, cyanogen, methane, other hydrocarbons, carbon monosulfide, carbon disulfide, carbonyl sulfide, etc., according to the other elements present. The first eight contain oxygen and are quantitatively converted to carbon monoxide under the proper conditions. Ammonia is removed from the gas stream by concentrated sulfuric acid, and acid gases are removed by sodium hydroxide. The exceptions are hydrogen fluoride and fluorine which react with the quartz tube and liberate oxygen during pyrolysis, giving high results. After the absorption of acidic and basic gases, the carbon monoxide passes through iodine pentoxide at 110°C,



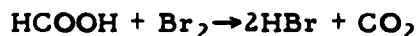
The iodine is absorbed in acetic acid which contains bromine and potassium acetate,



When water is added,



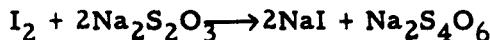
Excess bromine is removed by adding formic acid,



Next, potassium iodide is added:



The liberated iodine is titrated with 0.02 N sodium thiosulfate solution, starch being added near the end point,



Thus, the amount of iodine titrated is six times that released by the iodine pentoxide, presenting a very advantageous conversion factor. For each mole of oxygen present in the analyzed substance, 2.4 moles of iodine are finally available.

B. First Trial.

The pelletized carbon for microdetermination of oxygen was sieved and the 20-80 mesh (0.84 to 0.17 mm) size was washed with hydrochloric acid, dried, and placed in the platinum tube. Several extra microclamps were attached to the tube just beyond the furnace to give cooling by heat transfer. The results are shown in table 1 in the order in which successive runs were made.

TABLE 1
APPARENT OXYGEN IN VARIOUS COMPOUNDS
(Platinum Tube, HCl-Treated Carbon)

Compound	F (calcd)	O (calcd)	Apparent O (found)
%			
Benzoic acid	0.00	26.20	25.99
Teflon	75.98	0.00	11.09
Teflon	75.98	0.00	*
Teflon	75.98	0.00	5.48
Teflon	75.98	0.00	3.80
Perfluorodibutyl ether	75.32	3.52	5.50
Teflon	75.98	0.00	3.47
Teflon	75.98	0.00	3.00

* About a 100-mg sample to reduce impurities in carbon. Apparent oxygen was not determined.

The fluorine interference is less than that found by any quartz tube method used previously. It will be seen that the apparent effect of fluorine was decreasing but remained unacceptably high. It was, at this point, believed that high results were principally caused by trace silica in the carbon.

C. Second Trial.

Consequently, fresh hydrochloric acid-washed carbon was placed in 48% hydrofluoric acid, allowed to stand for 4 days, washed, dried, and resieved. The results from the use of this carbon are shown in table 2 in the order in which successive runs were made.

TABLE 2
APPARENT OXYGEN IN VARIOUS COMPOUNDS
 (Platinum Tube, HCl- and HF-Treated Carbon)

Compound	F (calcd)	O (calcd)	Apparent O (found)
Acetanilide	0.00	11.84	11.81
Teflon	75.98	0.00	7.21
Teflon	75.98	0.00	*
Teflon	75.98	0.00	3.48
Teflon	75.98	0.00	2.97
Teflon	75.98	0.00	2.20
Perfluorodibutyl ether	75.32	3.52	6.80
Teflon	75.98	0.00	*
Teflon	75.98	0.00	1.71
Teflon	75.98	0.00	*
Teflon	75.98	0.00	0.58
Teflon	75.98	0.00	0.18
Teflon	75.98	0.00	0.13
Perfluorodibutyl ether	75.32	3.52	4.51

* About a 125-mg sample to reduce impurities in carbon. Apparent oxygen was not determined.

Note that the apparent oxygen values of both fluorine compounds analyzed decrease toward the calculated value. The last two results on Teflon might be acceptable if subsequent determinations give similar values.

In an effort to quickly eliminate impurities in the carbon filling, dry hydrogen fluoride was passed through fresh carbon filling at 200°C for 16 hours. Before running any compounds containing fluorine, the tube developed leaks. Since similar tube damage had occurred once before during hydrogen fluoride treatment, it was concluded that attempts to purify the carbon in situ were ill advised. It also appears that treatment with hydrogen at high temperatures causes platinum to become porous.*

III. DISCUSSION.

Kirsten¹² reported that platinum inserts in a quartz pyrolysis tube were disintegrated by the carbon from the pyrolysis gases, forming platinum carbide. However, experiments on the platinum tube, carried out here, showed no such effect. The interior surface was still bright after many determinations. Crystallization could be observed on the outside surface; and a little, on the inside surface. No particular attack on the platinum foil ribbon, used here to support carbon in the quartz tubes, has been noted. This platinum ribbon can frequently be cleaned and used again.

One of the platinum tubes used in this work was operated at 1,120°C for 3 months without damage. However, at 200° to 300°C, hydrogen fluoride gas caused porosity to develop. It appears that the useful life of the platinum tube should be adequate, unless the tube is mistreated. If the tube develops leaks after long use, the porous section is cut out, the scrap platinum is recovered, and a new section is welded in place at small cost.

Whenever this method is discussed or presented to a group, a question is always asked about the cost of the platinum tube. The value of the platinum in the 1-kg tube is about \$3,000. The fabrication cost was \$100. The

* Shrinkage of the carbon particles also occurs in both platinum and quartz tubes during the purification with hydrogen. This shrinkage in itself is not harmful provided the tube is cooled and the carbon is packed down by shaking thoroughly, a normal procedure in this laboratory. If this repacking is omitted, a channel will be formed in the carbon after use, and low results will be obtained.

fabrication of a new section to replace a leaking one was \$15 in one instance and \$50 in another. The platinum is, of course, recoverable; and, while the initial cost for the pyrolysis tube is high, subsequent costs are not significantly higher than the cost of quartz-tube analysis.

IV. CONCLUSIONS.

It is believed that the platinum-tube method devised here shows good promise for eliminating the interference of fluorine in the oxygen determination. Further work is planned with other compounds and with carbon thoroughly purified before placing it in the platinum tube.

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